

Shear-Induced Crystallization in Isotactic PP Blends With Different Molecular Weight Distribution

A. Nogales, B. Hsiao, R. Somani (SUNY, Stony Brook), F. Balta-Calleja, T. Ezquerro (Instituto de Estructura de la Materia, Spain), S. Srinivas, A. Tsou (ExxonMobil Chemical Company)

Abstract No. Noga2111

Beamline(s): X27C

Introduction: *In-situ* SAXS (small-angle x-ray scattering) and WAXD (wide-angle x-ray diffraction) experiments were used to follow the structural and morphological developments of a series of isotactic polypropylene blends with different molecular weight distribution. The crystallization kinetics exhibits a strong dependence on the molecular weight distribution. The aim of this study was to investigate, more in detail, the role of the high molecular weight species on crystallization after step-shear. Only polymer chains above a 'critical orientation molecular weight' (M^*) can become oriented at a given shear rate; it was found that, regardless of MWD, a similar value for M^* is obtained under the present experimental conditions.

Methods and Materials: A series of blends containing two different molecular weight resins: one i-PP homopolymer of lower molecular weight (resin I), and second homopolymer of higher molecular weight (resin A) were used in this study. A Linkam CSS-450 high temperature shearing stage modified for *in-situ* x-ray scattering studies was used to precisely control shear-field and thermal history of the polymer (i-PP) samples. Synchrotron x-ray measurements were carried at the X27C beamline in NSLS; a 2D MAR CCD detector was used for the detection of 2D scattering patterns.

Results: The SAXS results show that development of oriented structures after the cessation of step shear (strain = 1428%, rate = 57 s^{-1}); however, the low molecular weight resin shows lower fraction of the oriented structures compared to the blends containing high molecular weight resin. The crystallization kinetics was determined from the SAXS intensity profiles (as well as the WAXS data); it was observed that, the addition of a very small amount of high molecular weight chains (4%) in i-PP of lower molecular weight was sufficient to induce a drastic change in the crystallization kinetics. The increase in crystallization rate after imposition of shear is mainly due to the formation of many primary nuclei through homogeneous nucleation process consisting of oriented chain aggregates, which greatly facilitate the kinetics of crystallization. The oriented fractions obtained by SAXS and the MWD data from GPC, for the different blends, was used to define the low end cut-off at critical orientation molecular weight (M^*). Figure 1 shows the molecular weight distribution curves for the two homopolymers and for a blend (containing 84% low molecular weight resin and 16% high molecular weight resin). The edges of the dotted lines indicate the two average limits for M^* obtained. The results suggest that the critical orientation molecular weight is independent of the molecular weight distribution. We propose a model for the structure development in I-PP after a brief pulse of shear at high strength in which, due to the applied deformation, a gradient of extension in high molecular weight tail species can develop. Molecules with high molecular weight can be significantly extended ($R_g^{\parallel} \gg R_g^{\perp}$), as the molecular weight decreases, the chain may be less extended, but still presenting a net orientation, characterized by ($R_g^{\parallel} > R_g^{\perp}$). Below a given critical orientation molecular weight, M^* , which apparently depends only on the shearing conditions (not on the MWD), the molecules cannot be oriented, and they give rise to a randomly distributed crystallinity.

Conclusions: Upon application of a step shear at 1428% strain with a shear rate of 57 s^{-1} , the WAXS patterns of different isotactic polypropylene melts at 150°C show development of oriented crystallites. Crystallization kinetics is influenced by the MWD; introduction of a very small amount of high molecular weight chains is sufficient to affect a drastic change in the kinetics. For a given shear rate, the critical orientation molecular weight, M^* , is found to be independent of molecular weight distribution.

Acknowledgments: The financial support for this project was partly provided by NSF DMR-9732653 and by DGICYT, Spain (grant PB-0049) and ExxonMobil Chemical Company.

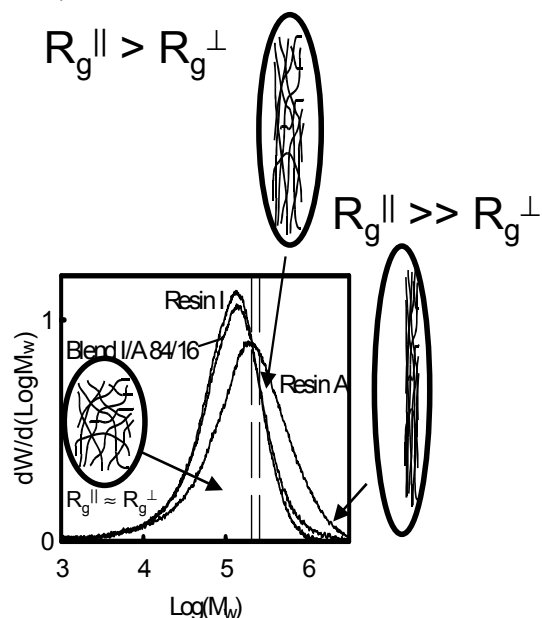


Figure 1. GPC patterns for I-PP resins, I (low molecular weight resin), A (high molecular weight resin), and I/A 84/16 blend. The dotted lines represent two limits for the critical orientation molecular weight.